# Section 3. Chemistry

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## PHOSPHORUS-SULFUR AND NITROGEN-PHOSPHORUS-SULFUR COMPLEXES BY ACTIVATING PHOSPHORITES WITH SULFURIC AND NITRIC ACIDS IN THE PRESENCE OF SULFUR

**Abtract.** It was studied that it is possible to obtain complex phosphorus-sulfur and nitrogen-phosphorus-sulfur fertilizers with insecticidal properties necessary for agriculture by reprocessing low-grade Kyzylkum phosphorites in the presence of sulfur with incomplete standards of sulfuric and nitric acid. 30–40% of acid consumption is saved by replacing the amount of sulfur in the sulfuric acid used in the decomposition process with elemental sulfur. The received fertilizers contain phosphate minerals in mono- and dicalcium phosphate form, and sulfur in $SO_4^{2-}$ ion and elemental form. It was found that the sulfur in the fertilizer is in a completely hydrophilic form.

**Keywords: l**ow-grade phosphorite, nitrogen-phosphorus-sulfur fertilizer, insecticide, technological scheme.

**Introduction**

Among the insecticides, sulfur containing drugs are not harmful to humans and livestock. Lime: sulfur (2:1) decoction (ISO), sulfur talc, colloidal sulfur are used as sulfur insecticides: However, the process of obtaining these insecticides is complex and requires a lot of energy and finance.

Scientists around the world, including in Uzbekistan are looking for low-cost and resource-efficient ways to obtain phosphate fertilizers from unenriched and low-quality phosphorites. In this regard, promising scientific research shows that a new type of complex fertilizers has been developed by activating phosphorites on the basis of chemical, mechanical, mechanochemical, thermal and bacterial means [1–2].

Therefore, one of the most pressing issues today is the development and implementation of specific resource-saving technologies for the production of phosphorus-sulfur and nitrogen-phosphorus-sulfur complex fertilizers containing insecticides that fight disease-causing insects, along with phosphorus feed. The application of these phosphorus-sulfur fertilizers simultaneously provides the plants with nutrients and protects them from various diseases.

The material significance of phosphate minerals in the Central Kyzylkum basin began to be studied by scientists by 1960 s. Phosphate minerals in the Kyzylkum basin cover an area of 65.000 $km^2$. Only 10% of granular phosphorites with a total volume of 10 billion tons can be mined opencast. The Geroy, Sardara, Tashqura, Qaraqat, and Jetimtog deposits in the Kyzylkum basin have been studied almost completely. The Jeroy-Sardara phosphorite deposit, one of the largest deposits, has reserves of 2.9–3.0 billion tons. (550 million tons $P_2O_5$). Of this, phosphate mineral reserves with an average content of 19.42 % $P_2O_5$ estimated to 223.9 mln. tons (43.5 million tons $P_2O_5$). This phosphorite reserve can be the basis for the supply of phosphate fertilizers to agriculture of the republic for 62 years. The Kyzylkum phosphorite complex was also built around this deposit.

Phosphorite reserves of Tashkura deposit are estimated at 1.1 billion tons. (200–250 million tons $P_2O_5$). The reserves of the Karakat field are estimated at 600–650 million tons. $P_2O_5$ (3.0–3.5 billion tons ore). Of this, 55–60 mln. tons $P_2O_5$ (320 million tons of ore) is located at a depth of 60 m.

Two top layers of phosphorite 1–1.3 m in width across the horizon are of industrial importance. They are separated from each other by weak phosphated marl layers of 8–12 m. The amount of $P_2O_5$ in the phosphorite is 16–19% in the first layer and 21–23% in the second layer. The results of chemical and physicochemical analysis revealed that the composition of Kyzylkum phosphate raw materials consists mainly of the minerals fluorocarbonatapatite and calcite.

Petrographic data show that Sardara area phosphorites are composed of granular organogenic-koolithic residues. In the surface part of the Paleocene and Eocene Cretaceous mixed deposits, types of phosphorites such as granular (Africa), shell (Chilisoy) and sandstone (Florida) have been identified.

Ore phosphated grains and coolite phosphates, which are organic residues, are composed of cement carbonates with about 70% and small amounts of clay additives. The results of mineralogical studies have shown that the composition of granular phosphorite ores is similar to each other. It is composed of 10% to 90% phosphate minerals, the rest being calcite, montmorillonite, hydromica, polygorskite, hydrogenite, quartz, gypsum, glauconite, feldspar and halite minerals [3–10].

Non-phosphated minerals include calcite (20–50%), montimorillonite, hydromica and polygorskite, hydrogemit (0.1–15%), gypsum (5–10%), quartz (0.1–70%), glauconite (residues). feldspar (0.1–0.3%) and halites. Iron residues in minerals occur in the form of yellow sulfide, hydroxide up to 12%. Clay carbonated phosphates have higher iron content and higher carbonate phosphorites have lower iron content. The main part of magnesium is in montmorillonite, and a small amount is in dolomite.

Average mineralogical composition of ore deposits (heavy fraction%); francolite-56.0, calcite-26.5, quartz-7.5–8.0, hydraulic minerals and feldspar 4–5, gypsum-3–5, getite-1, zeolite 1.0, and organic components are about 0.5.

The phosphate mineral in donor phosphorite corresponds to carbonatophthorapatite, known in the literature as "kurskit". The average chemical composition of the phosphate mineral (%) is $P_2O_5$–32.10; CaO-48.37; $CO_2$–5.0; F-3.19; MgO-0.04; $Al_2O_3$–0.2; $Fe_2O_3$; $Na_2O$-0.10; $K_2O$-0.05; $SO_3$–0.08; $SiO_2$ is 0.05.

Currently, scientists are proposing to produce a variety of phosphate fertilizers that are chemically activated by phosphorites and have a gradual effect. Activation of phosphorites with high carbonate content increases the contact surface of phosphate particles due to their decarbonization. As a result, phosphorite is converted into a plant-assimilating form. There is a growing need to implement an accelerated technology for the production of low-cost, highly agrochemically efficient fertilizers through chemical activation of low-quality and unenriched phosphorites. At the same time, the urgency of obtaining complex fertilizers using various mineral acids, mineral salts used in agriculture, i.e. mineral fertilizers, etc., increases.

Scientific studies of the processing of Kyzylkum phosphorites have shown that it has a high ability to undergo chemical reactions. This requires the need to obtain high-efficiency complex fertilizers with intensive technology without spending large activation energy to convert phosphate raw materials into plant-assimilating form.

**Experimental**

In order to develop a scientific basis for the production of new varieties of insecticidal phosphorus-sulfur fertilizers from local raw materials, the process of decomposition of enriched phosphorite flour and low-quality phosphorite samples with incomplete norms of sulfuric acid in the presence of sulfur was studied. In order to determine the optimal conditions for the decomposition process, a mixture of phosphorite and sulfur with a ratio of 1: 0.001–0.2 was studied using 75, 80 and 93% solutions of sulfuric acid and at a rate of 60–90%. The amount of sulfuric acid consumed was calculated relative to the formation of calcium dihydrogen phosphate and calcium sulfate by breaking down the phosphate and calcite minerals in the phosphorite samples. Laboratory experiments were performed as follows. Samples of phosphorite and sulfur mixtures are mixed with a solution of sulfuric acid simultaneously for 15–20 minutes. Since the interaction reaction of the components is exothermic, it was observed that the temperature is 70–120 °C and higher depending on the acid norm. The heat released is used to evaporate excess water in the system, leading to an improvement in the commercial properties of phosphorus-sulfur fertilizers. After the finished product was cooled and classified, its components were chemically analyzed using certain standard methods. In order to develop a scientific basis for the production of complex phosphorus-sulfur fertilizers, the process of processing phosphate raw materials in the presence of a suspension of sulfuric acid was studied.

75%, 80% and 93% solutions of sulfuric acid were used in the study. Sulfur suspensions of these concentrated acids were prepared under laboratory conditions. Increasing the acid concentration has a positive effect on the hydrophilization of sulfur. This is because the non-polar molecules of sulfur tend to form a hydrophilic form only in non-polar solvents. A decrease in the acid concentration leads to an increase in the mass fraction of water in the solution. Water is a polar molecule.

Under the action of sulfuric acid molecules, it oxidizes to form a suspension of sulfuric acid. Phosphorite samples were processed through this suspension.

Initially, on the basis of intensive technology, the process of decomposition of unenriched phosphorite flour with different standards of suspension containing 93% sulfuric acid solution with 3.5 and 7.5% sulfur was studied. Sulfuric acid was the norm in stoichiometry, which was used to break down phosphate and carbonate minerals in phosphorite to form calcium dihydrogen phosphate and calcium sulfate. The process of processing phosphorite flour with sulfuric acid was carried out as follows. In the reactor, 0.1–0.3 kg of raw phosphorite was mixed continuously with the sulfuric acid suspension for 20–30 min. After cooling and classification of the obtained product, the various forms of $P_2O_5$ and total CaO, $CO_3$, moisture content were analyzed using certain standard methods.

**Results and discussion**

The results of the analysis showed that the activation of phosphorite, ie the decomposition coefficient, increases with increasing sulfur content in the processing of phosphate raw materials. For example, with a 1: 0.001 ratio of phosphorite and sulfur, 59.66% of the total $P_2O_5$ in the processed product with 93% sulfuric acid is converted into a plant-assimilating form, and 48.76% into a water-soluble form. Also, the 1: 0.01, 1: 0.05, and 1: 0.15 ratios of phosphorite and sulfur were compared to the 1: 0.001 ratio, respectively, while the plant-absorbing part was 1.02, 2.21, and 1.46 times, respectively, while the water-soluble form was 1.01, 1.03, and 1.12 times. This bond is maintained in both 70 and 80% solutions of sulfuric acid. However, the rate of decomposition of phosphorite flour with sulfuric acid in the presence of sulfur varies depending on the acid concentration, i.e., a decrease in the acid concentration leads to a decrease in its decomposition coefficient. For example, when a mixture of phosphorite and sulfur in a ratio of 1:0.01, 1:0.05 and 1:0.15 is processed at a rate of 60% of an 80% solution of sulfuric acid, the plant absorption fraction is 1, respectively, compared to a 93% solution of acid. 06, 1.12 and 1.19, while the water-soluble form decreased by 1.38, 1.35 and 1.39 times, respectively. In a 75% solution of the acid, the plant assimilation form decreases by 1.08, 1.15 and 1.25 times, and the water-soluble part by 1.50, 1.46 and 1.48 times.

When phosphate raw materials are processed with sulfuric acid in the presence of sulfur, we see that the decomposition coefficient is 1.2–1.3 times higher when compared with the sulfuric acid.

The process of processing a sulfur mixture of low-quality phosphorites with sulfuric acid is practically no different from that of unenriched phosphorite flour, i.e. the above mechanism is preserved. For example, when a 1:0.05 ratio of phosphorite and sulfur is processed in a 93% sulfuric acid solution at 60, 70, and 80%, the decomposition rate of the raw material is 62.42%, 73.20%, and 77.84%, respectively 36.92%, 39.98% and 43.83% in aqueous solution. This enriched phosphorite showed that the absorbent $P_2O_5$ fraction was 1.07, 1.09, and 1.17 times lower, and the water-soluble form 1.36, 1.35, and 1.32 times lower, respectively. This is because the content of low-quality phosphorite is slightly higher than that of carbonates and the grain content varies.

At incomplete rates of sulfuric acid, a certain proportion of phosphate minerals remain undigested. Under the influence of acid molecules, the crystal lattices of phosphate minerals in the raw material undergo changes. Phosphates that do not decompose due to defects in the crystal lattice nodes of minerals are converted into plant-absorbing phosphates as a result of oxidation of sulfur to form a weakly acidic environment.

The obtained fertilizers contain phosphorus in the form of mono- and dicalcium phosphates, and sulfur in the form of $SO_4^{2-}$ ions and elemental sulfur. These results are also confirmed by X-rays and dervatograms of the fertilizer obtained.

Under the influence of sulfuric sulfuric acid, the phosphate raw material decomposes quickly (in 5–10 minutes) and easily. The carbon dioxide and fluorine compounds released during decomposition accelerate the diffusion of phosphate particles with the hydrogen ions of the acid. Since the decomposition reaction is exothermic, it was observed that the temperature was 70–120 °C and higher depending on the sulfuric acid norm. The heat released is used to dry the sulfur superphosphate.

The results of the study are presented in Table 1. The results showed that the rate of decomposition of phosphorite minerals also increases as the rate of sulfuric acid used for phosphorite processing increases. For example, in the processing of unenriched phosphorite, the stoichiometric rate of acid changes from 60% to 100%, the plant absorption of total phosphorus in the product increases by 1.46 times, and the water-soluble part increases by 1.40 times.

Decomposition of unenriched phosphorite flour in different proportions of sulfuric acid suspension differs by the fact that the amount of sulfuric acid used in traditional classical methods is economical and has insecticidal properties as free sulfur in the composition of the resulting fertilizer. The product formed by the reaction of phosphorite with sulfuric sulfuric acid is always broken down into fine particles during the mixing process and is exposed to the phosphate raw material that is not involved in the reaction. At the same time, phosphate raw materials continue to be activated due to sulfur in the system.

The process of decomposition of phosphorite continues even after the fertilizer is applied directly to the soil, as a result of oxidation of sulfur in the soil under the influence of oxidizing microorganisms. Simultaneously with the phosphate mineral, the calcite in the raw material is also broken down. As the acid norm increases, so does its rate of decomposition. The sulfur in the product has a positive effect on the decomposition rate of phosphorite. During the interaction of the components, part of the sulfur is oxidized to acid and it actively participates in the decomposition of minerals. The sulfur in the new fertilizer becomes hydrophilic.

As a result of exposure of phosphorite to a 3.5% sulfuric acid suspension at a rate of 60%, 14.52% of the total $P_2O_5$ is converted to a plant-assimilated form. Also, at the 70 and 90% norms, the plant-assimilating $P_2O_5$ fraction increases 1.17 and 1.42 times, respectively, compared to the 60% norm. The product obtained from the decomposition of unenriched phosphorite flour in the presence of a suspension of 7.5% sulfuric acid, compared with a suspension of 3.5% sulfuric acid, the plant assimilation form of phosphorus in the raw phosphate averaged 1.02 times, and on average 1.25 times in the unused sample. showed that it is high.

The amount of water in the sulfuric acid used in the decomposition of phosphorite flour affects the granularity of phosphate fertilizers. The high amount of water in the suspension, ie the low acid concentration, complicates the process and the product is obtained with unsatisfactory brand properties. When enriched phosphorite is processed at 60–80% of sulfuric acid stoichiometry, a powdery product is obtained. Its content of grains with a size of 1–3 mm is 30–40%. Under the influence of 80–100% of sulfuric acid, a new phosphorus fertilizer with a size of –3 – + 2mm and –2 – + 1mm, with an average grain size of 70–90% is obtained.

Table 1. – Decomposition of unenriched phosphorite flour with a suspension of sulfuric acid

| $H_2SO_4$ norm,% | Quantitative composition of $P_2O_5$,% | | | $CO_2$,% | $S_{total.,\%}$ | $S_{el.,\%}$ | $\frac{P_2O_5\ used.}{P_2O_5\ total}$ | $\frac{P_2O_5\ used.}{P_2O_5\ total}$ | $H_2O$,% | $K_{dekarb.}$,% |
|---|---|---|---|---|---|---|---|---|---|---|
| | general | assimilation | watery | | | | | | | |
| 3.5% sulfuric acid | | | | | | | | | | |
| 60 | 14.42 | 9.74 | 7.71 | 4.51 | 10.86 | 1.08 | 67.54 | 53.47 | 0.46 | 70.04 |
| 70 | 13.87 | 10.91 | 7.98 | 3.01 | 12.17 | 1.22 | 78.65 | 57.53 | 0.61 | 80.26 |
| 80 | 13.26 | 11.93 | 8.96 | 1.22 | 13.30 | 1.33 | 89.97 | 67.57 | 0.78 | 92.00 |
| 90 | 12.68 | 12.13 | 9.12 | 0.82 | 14.38 | 1.43 | 95.66 | 71.92 | 0.90 | 94.62 |
| 100 | 12.22 | 12.09 | 9.17 | 0.28 | 15.30 | 1.53 | 98.94 | 75.04 | 1.04 | 98.16 |
| 7.5% sulfuric acid | | | | | | | | | | |
| 60 | 14.29 | 9.76 | 7.72 | 4.40 | 12.07 | 2.40 | 68.30 | 54.02 | 0.40 | 71.15 |
| 70 | 13.61 | 10.81 | 7.91 | 2.84 | 13.43 | 2.67 | 79.43 | 58.15 | 0.47 | 81.38 |
| 80 | 13.00 | 11.70 | 8.87 | 1.17 | 14.65 | 2.91 | 90.00 | 68.23 | 0.71 | 92.33 |
| 90 | 12.44 | 11.97 | 9.01 | 0.51 | 15.77 | 3.14 | 96.22 | 72.43 | 0.81 | 96.65 |
| 100 | 11.98 | 11.87 | 9.10 | 0.19 | 16.88 | 3.37 | 99.08 | 75.96 | 1.03 | 98.75 |

Table 2. – Physical and mechanical properties of phosphorus-sulfur fertilizer grains

| $S_{el.}$,% | $H_2O$,% | Volumetric weight, g/sm³ | Strength, *MPa/sm²* | Flowability, % | Natural angle of slope, ° | Fluidity, *s* | Hygroscopic point,% |
|---|---|---|---|---|---|---|---|
| 3.5% sulfuric acid | | | | | | | |
| 1.08 | 1.25 | 0.81 | 1.61 | 100 | 39 | 18.71 | 77 |
| 1.22 | 1.19 | 0.81 | 1.67 | 100 | 40 | 17.98 | 76 |
| 1.33 | 1.12 | 0.83 | 1.73 | 100 | 41 | 16.89 | 75 |
| 1.43 | 1.04 | 0.88 | 1.78 | 100 | 42 | 15.98 | 73 |
| 1.53 | 0.98 | 0.96 | 1.86 | 100 | 42 | 15.07 | 73 |
| 7.5% sulfuric acid | | | | | | | |
| 2.40 | 1.23 | 0.82 | 1.66 | 100 | 40 | 18.52 | 76 |
| 2.67 | 1.16 | 0.82 | 1.72 | 100 | 41 | 17.02 | 74 |
| 2.91 | 1.09 | 0.83 | 1.78 | 100 | 42 | 16.72 | 73 |
| 3.14 | 1.02 | 0.90 | 1.84 | 100 | 42 | 15.77 | 73 |
| 3.37 | 0.95 | 0.97 | 191 | 100 | 42 | 15.05 | 72 |

In order to further improve the physical-mechanical and commodity properties of sulfur-phosphate fertilizers, the process of granulation of them in the presence of a 40% solution of ammonium sulfate was studied. The new fertilizer obtained in a plate granulator was dried 2–3 mm grains and their properties were studied. Physico-mechanical properties of granulated phosphorus-sulfur fertilizers are given in (Table 2).

The possibility of intensive processing of new multifunctional complex fertilizer by processing enriched phosphorite flour with a suspension of sulfuric acid, the properties of the fertilizer fully meet the requirements for use in agriculture.

In subsequent studies, phosphorite samples were processed with a suspension of sulfur in acid at different rates in order to reduce the amount of sulfuric acid consumption. The consumption of sulfuric acid required for the decomposition of phosphorite was reduced from 100% to 60% of the norm. It was calculated that the bound sulfur in the sulfuric acid content was replaced by the corresponding elemental sulfur to cover the reduced acidity. A sulfuric acid suspension was prepared by mixing the sulfur calculated in the stoichiometric norm with concentrated sulfuric acid.

The chemical composition of the new variety of fertilizer, which was processed phosphorite with a suspension of sulfuric acid ($H_2SO_4$ + + S), was analyzed by analyzing the chemical composition, ie the amount of $P_2O_5$ in different states. Hydrophilicity of sulfur, degree of decarbonization of phosphorite and CaO were also determined. Incomplete decomposition of unenriched phosphorite flour with sulfuric acid has been shown to have no adverse effect on product quality when elemental sulfur is used instead of acid-bound sulfur. For example, when decomposed in the presence of sulfuric acid, 98.24% of the total $P_2O_5$ in the fertilizer content of 11.38% is converted into plant-assimilating and 72.95% into water-soluble $P_2O_5$

When 5%, 20% and 40% of the sulfuric acid bound sulfur is replaced by elemental sulfur, the amount of plant-absorbing $P_2O_5$ in the new variety of fertilizer is 1.01, 1.04 and 1.19 times, respectively, and the solubility in aqueous solution is 1.02, 1., Decreased by 10 and 1.39 times, respectively. This indicates that the decomposition coefficient values of the phosphate mineral have not changed dramatically. The sulfur in the resulting fertilizer is 100% hydrophilic.

In the process of obtaining low-quality phosphorite fertilizer processed with sulfuric acid, the bonds observed in the unenriched phosphorite flour are preserved. When the sulfuric acid content is reduced to 40%, 81.12% of the total $P_2O_5$ content of 11.12% is plant-assimilating and 47.87% is water-soluble.

The acid consumption is saved by 30–40% when the sulfur sulfate we propose is decomposed under the influence of an acid suspension. As a result of the addition of sulfur to the composition of complex phosphate fertilizers, the amount of nutrients increases and has an insecticidal effect.

Different rates of nitric acid and their decomposition process in the presence of sulfur were studied to obtain insecticidal complex fertilizers containing NPSCa nutrients from low-grade unenriched phosphorites [29–30].

The stoichiometric 20–60% content of 57% nitric acid for the decomposition of phosphorite samples was calculated relative to the formation of monocalcium phosphate and calcium nitrate salts from the decomposition of carbonate and phosphate minerals in the raw material.

In order to study the effect of sulfur on the decomposition of phosphorite samples in the presence of nitric acid, phosphorite containing 10% sulfur was decomposed with nitric acid.

During the decomposition of phosphorite, the temperature varies in the range of 30–45 °C depending on the acid norm. The resulting complex fertilizer was dried at a temperature of 100–−105 °C.

The results of the chemical analysis of the composition of the formed fertilizers show that the decomposition rate of low-grade phosphorites varies depending on the acid norm. For example: enriched phosphorite is broken down under the influence of 20–60% of nitric acid, 9.03–12.03% of the total $P_2O_5$ in NPSCa complex fertilizer is 28.44–77.19% in the form of plant assimilation. The decarbonization rate rises from 30.76% to 81.89%, respectively. When the obtained fertilizers are analyzed after drying, 10.78–12.92% of the total $P_2O_5$ is 29.80–80.06% in plant assimilation form. It also contains 2.67–– 6.90% nitrogen, 30.06–35.58% calcium oxide, 6.43–8.10% elemental sulfur, 1.34–2.11% water.

Also, the conversion of sulfuric acid to sulfuric acid in NPSSa complex fertilizer decomposed into a sample containing 10% sulfur of unenriched phosphorite flour with a range of 20% to 60% of nitric acid increases with increasing acidity. For example: 10.15% of the total 8.94% of total sulfur is converted to sulfuric acid at a rate of 20%. When the nitric acid norm is 30 and 50%, the rate of conversion of sulfur to sulfuric acid is 1.24 and 1.32 times higher than the 20% norm, respectively. The sulfur remaining in the elemental state in the fertilizer is in a completely hydrophilic form.

The decomposition process of low-quality phosphorites in the presence of sulfur with nitric acid is practically no different from that of non-enriched phosphorites. The decomposition coefficient of low-quality phosphorite is 1.33 times lower than that of unenriched phosphorite.

This difference can be explained by the fact that the granular composition of low-quality phosphorite is different.

Nitric acid is not only a source of chemical energy for the decomposition of phosphate minerals in the raw material, but also participates in the process of mutual oxidation-reduction of components in the system (phosphorite, sulfur, nitric acid, moisture, etc.). Under these conditions, elemental sulfur is oxidized from $S^0$ to $S^{+4}$ ($S^{+6}$) and converted to sulfite and sulfuric acid in the system. When phosphorites are processed with nitric acid in the presence of sulfur, the decomposition coefficient is 1.45 times higher than that of nitric acid. The change in this indicator can be expressed as follows.

During processing, the undigested part of the phosphorites continues to be activated by the weak acidic environment formed in the crystal lattice system. The product contains salts of calcium hydrophosphate and calcium sulfate. Additional $SO_4^{2-}$ ions in the reaction products begin to form in the form of gypsum.

Commodity properties of products obtained from more than 40% of acid standards do not meet agricultural requirements.

Unenriched phosphorite flour is 19.118% of the total $P_2O_5$ in the complex fertilizer composition processed under the influence of 20% norm of 57% nitric acid in the form of plant assimilator $P_2O_5$. The decarbonization rate of phosphorite flour is 22.62%.

The process of processing sulfur phosphorite with nitric acid also occurs rapidly. Scientific studies have shown that as the amount of sulfur in phosphorite increases, so does the rate of decomposition of the raw material. For example, the decomposition rate of phosphorite containing 1% sulfur is 1.04 times that of a sample treated with 20% nitric acid, and the degree of decarbonization is We observe an increase of 1.06 times. During the decomposition of phosphorite flour, an increase in sulfur content of 5, 10 and 30% was observed to increase the nutrient value of assimilated phosphorus in NPSCa fertilizers by 1.25, 1.39 and 1.54 times, respectively.

When the content of sulfur in the content of unenriched phosphorite flour is from 1% to 30%, when processed at the rate of 30% of nitric acid, 9.34–12.04% of the total $P_2O_5$ is 37.69–60.17% in the form of plant assimilation. When 40% of nitric acid is used in this process, 8.70–11.08% of the total $P_2O_5$ is in the plant-assimilated form of 47.36–65.40%.

After the product dries, these values increase 1.12–1.30 times due to water loss. The increase in the decomposition rate of unenriched phosphorite flour in the presence of sulfur can be explained by an increase in the value of $SO_3$ in the obtained fertilizers (Fig. 1). For example, when a phosphorite sample is processed at 30% nitric acid without sulfur, it contains 1.65% $SO_3$, and when treated with 5 and 10% sulfur, its value is 3.85 and 5.32%, respectively.

Based on the results of the study, it was proved that it is possible to process enriched phosphorite flour in the presence of sulfur in an incomplete amount of nitric acid using an intensive method to obtain complex fertilizers containing multifunctional NPSCa.

A number of physical and mechanical properties of phosphorus-sulfur fertilizers were studied, including hygroscopicity, granular composition, grain strength, natural slope angle, bulk density, salinity and moisture content. Because these properties are associated with the efficiency of their storage, transportation, use in agriculture.

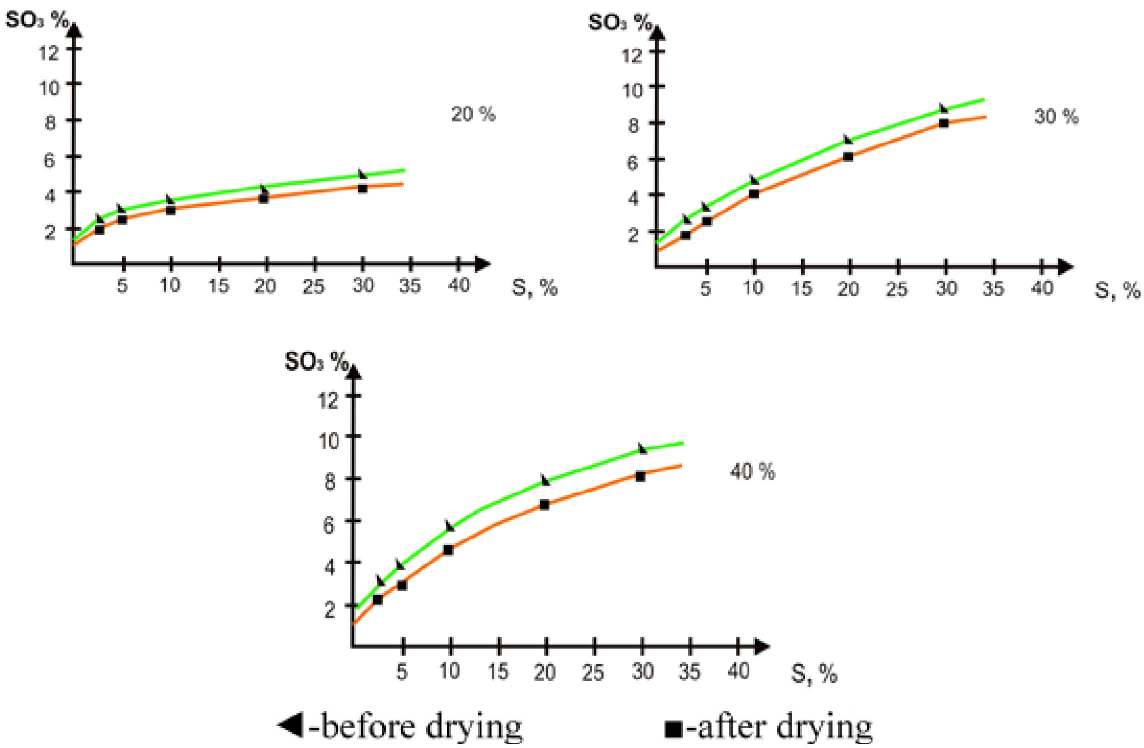


Figure 1. Formation of $SO_3$ in the decomposition of nitric acid in the presence of sulfur in enriched phosphorite flour with norms of 20, 30 and 40%

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To determine the viscosity of phosphorus-sulfur and nitrogen-phosphorus-sulfur fertilizers, specific mass fertilizer samples are placed in special cylinders and stored under loaded mass for twenty-four hours. The product is slowly pushed out of the cylinder and inspected under the force required to spray it. Studies have shown that under the conditions studied, not all fertilizer samples are sticky, i.e., friable.

It is important that the product is sufficiently crumbly and granular to achieve full utilization of the necessary nutrient components of the plant. The granularity of fertilizers leads to an increase in the agrochemical efficiency of agricultural crops.

The granular composition of the obtained insecticidal phosphorus-sulfur fertilizers was determined. The data obtained are presented in Table 3. The results show that the small-sized fractions in the fertilizer samples do not exceed 15%.

Table 3. – Granular composition of fertilizer samples

| **Fertilizer samples** | **Amount of fractions mm, weight%** | | | | |
|---|---|---|---|---|---|
| | **–5 +3** | **–3 +2** | **–2 +1** | **–1 +0.5** | **0.5 >** |
| ***1*** | ***2*** | ***3*** | ***4*** | ***5*** | ***6*** |
| Unriched phosphorite flour | | | | | |
| PS fertilizer $P_2O_{5tot.}$ – 16.32%, $S_{tot.}$ – 10% | 4.07 | 22.10 | 24.31 | 38.45 | 11.07 |
| PS fertilizer $P_2O_{5tot.}$ – 13.27%, $S_{el.}$ – 2.60% | 15.12 | 18.42 | 31.25 | 29.18 | 6.03 |
| PS fertilizer $P_2O_{5tot.}$ – 12.54%, $S_{el.}$ – 2.68% | 13.11 | 30.02 | 27.03 | 24.53 | 5.31 |
| NPS fertilizer N – 4.19%, $P_2O_{5tot.}$ – 13.04%, $S_{el.}$ – 3.73% | 14.86 | 19.23 | 38.61 | 24.95 | 2.35 |
| Low quality phosphorites | | | | | |
| PS fertilizer $P_2O_{5\,tot.}$ – 14.22%, $S_{tot.}$ – 10% | 5.18 | 20.44 | 23.00 | 38.75 | 12.63 |
| PS fertilizer $P_2O_{5\,tot.}$ – 10.60%, $S_{el.}$ – 2.79% | 16.27 | 17.26 | 28.19 | 30.98 | 7.93 |

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| PS fertilizer $P_2O_{5\,tot.}$ – 11.12%, $S_{el.}$ – 2.82% | 15.42 | 26.31 | 26.01 | 25.15 | 7.11 |
| NPS fertilizer N – 3.67%, $P_2O_{5\,tot.}$ – 12.14%, $S_{el.}$ – 4.41% | 16.17 | 18.92 | 37.77 | 22.54 | 4.96 |

The moisture absorption rate of fertilizers and their hygroscopicity were determined under conditions of relative humidity of 50, 85 and 100% in desiccators. The moisture absorption kinetics curves of fertilizers obtained in the presence of sulfuric acid and sulfur are practically the same. The process of moisture absorption of the product takes place on average 1–1.5 days and its value is 1.5–2.5%.

Fertilizers obtained in the presence of nitric acid and sulfur, the equilibrium in the relative humidity of the studied air takes place in an average of 10–12 days, and their value is 20–25%. PS fertilizers obtained in the presence of sulfuric acid and sulfur are not hygroscopic. Even if they are stored for a long time in different seasonal conditions, they do not lose their brand properties. The complex fertilizer with PSN obtained in the presence of nitric acid and sulfur attracts more moisture due to the formation of calcium nitrate, ie it is hygroscopic. It is therefore recommended to store them in special inner polyethylene-lined bags.

Based on the research, the composition of phosphorite samples was calculated from the basic salts in complex fertilizers with insecticidal properties, processed in the presence of sulfuric, nitric acids and sulfur. These values, calculated on the basis of chemical analyzes, are given in Tables 4–6.

Table 4. – Amount of salts in phosphorus-sulfur fertilizers obtained using incomplete norms of sulfuric and sulfuric acids,%

| Salts | Total | Components | | | |
|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | $SO_3$ | $CO_2$ |
| $Ca_5(PO_4)_3F$ | 6.88 | 3.54 | 3.72 | – | – |
| $Ca(H_2PO_4)_2$ | 11.09 | 6.73 | 2.66 | – | – |
| $CaHPO_4$ | 4.77 | 2.49 | 1.79 | – | – |
| $CaCO_3$ | 10.05 | – | 5.63 | – | 4.42 |
| $CaSO_4$ | 48.27 | – | 19.88 | 28.39 | – |
| S | 5.55 | – | – | – | – |
| Additional substances | 13.19 | – | – | – | – |
| Total | 100 | 12.76 | 33.86 | 28.39 | 4.42 |

Table 5. – Amount of salts in phosphorus-sulfur fertilizers obtained by suspension of sulfuric acid,%

| Salts | Total | Components | | | |
|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | $SO_3$ | $CO_2$ |
| 1 | 2 | 3 | 4 | 5 | 6 |
| $Ca_5(PO_4)_3F$ | 4.30 | 2.21 | 2.33 | – | – |
| $Ca(H_2PO_4)_2$ | 10.85 | 5.58 | 2.60 | – | – |

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| $CaHPO_4$ | 7.12 | 3.74 | 2.93 | – | – |
| $CaCO_3$ | 6.05 | – | 2.39 | – | 2.66 |
| $CaSO_4$ | 46.43 | – | 19.12 | 27.31 | – |
| S | 4.08 | – | – | – | – |
| Additional substances | 21.17 | – | – | – | – |
| Total | 100 | 12.54 | 30.37 | 27.31 | 2.66 |

Table 6.– Amount of salts in NPS fertilizers obtained using incomplete norms of sulfuric and nitric acid,%

| Salts | Total | Components | | | | |
|---|---|---|---|---|---|---|
| | | $P_2O_5$ | N | CaO | $SO_3$ | $CO_2$ |
| $Ca_5(PO_4)_3F$ | 12.48 | 6.42 | – | 6.67 | – | – |
| $Ca(H_2PO_4)_2$ | – | – | – | – | – | – |
| $CaHPO_4$ | 10.06 | 6.10 | – | 4.15 | – | – |
| $CaCO_3$ | 12.68 | – | – | 10.10 | – | 5.58 |
| $CaSO_4$ | 8.54 | – | – | 3.52 | 5.02 | – |
| $Ca(NO_3)_2$ | 23.55 | – | 4.02 | 8.04 | | – |
| S | 7.58 | – | – | – | – | – |
| Additional substances | 25.41 | – | – | – | – | – |
| Total | 100 | 12.52 | 4.02 | 37.20 | 5.02 | 5.58 |

Calculations showed that the main part of the fertilizer consists of calcium dihydrogen phosphate, calcium hydrophosphate and sulfur, which is not fully involved in the reaction, as well as phosphate minerals that have been activated.

Unprocessed phosphorite flour was processed with incomplete sulfuric or nitric acid in the presence of sulfur, and a technological system for the production of new insecticidal phosphorus-sulfur and nitrogen-phosphorus-sulfur complex fertilizers was developed.

These technological processes consist of the following stages:

- Department of reception, storage and transfer of phosphorite and sulfur raw materials;
- Department of reception, storage and transmission of mineral acids (sulfur, nitrate);
- Phosphorite decomposition, granulation and drying department;
- Department of preparation of binder solutions for granulation of the finished product;
- Department of dust and gaseous waste storage and treatment;
- Department of transportation, storage and packaging of finished products.

The main components of the new sulfur phosphorus fertilizer are mono- and dicalcium phosphates, various hydrated calcium sulfates and undigested active phosphorite.

The peaks in the distances between the planes are calcium sulphates in the d, Å 2.48, 2.18, 1.51, 2.06 $CaSO_4$, $CaSO_4 \cdot 0.5H_2O$ states, d, Å 1.97, 1.87, 1.85, 1.81, 1.79 $CaHPO_4 \cdot 2H_2O$, d, Å 2.25, 1.65. containing dicalcium phosphates and d, va 1.76, 1.59, 1.51 $Ca(H_2PO_4)_2$, d, Å 3.38, 3.01, 2.74, 2.58, 1.58 $Ca(H_2PO_4)_2 \cdot H_2O$ were found to be suitable for monocalcium phosphates. Other diffraction lines in the product represent unaffected active phosphorite particles.

The above-mentioned correlations remain even when the product samples are analyzed after drying. During the drying period, we observe that the decomposition rate of phosphorite increased by 1.02–1.06 times. The resulting fertilizer contains 3–4% N in the form of calcium nitrate, 10–13% $P_2O_5$ – calcium hydrophosphate and activated phosphorite, 1–24% elemental C, 25–35% Ca O.

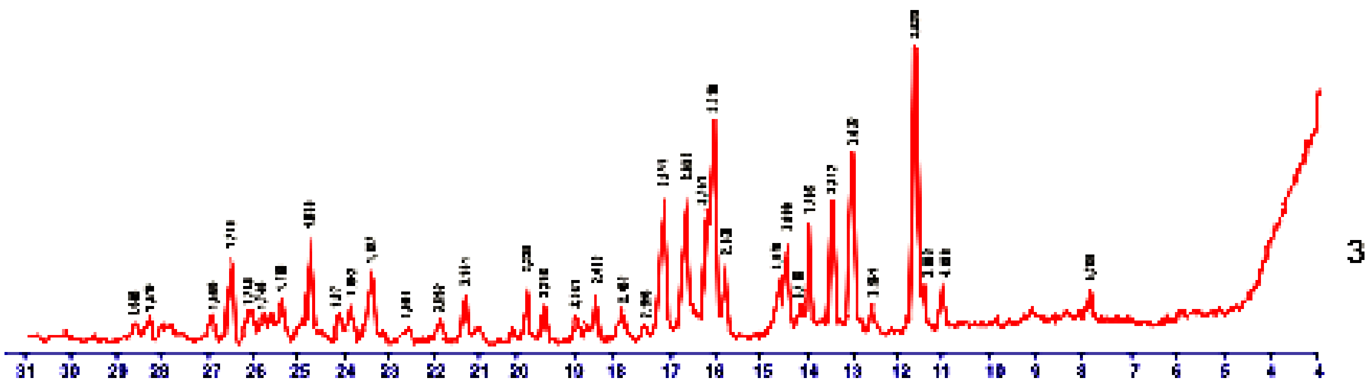

Figure 2. Powder X-ray diffraction pattern of complex NPSCa fertilizer

**Conclusions**

It was studied that low-grade Kyzylkum phosphorites can be processed in a short time with incomplete norms of sulfuric and nitric acids in the presence of sulfur to obtain complex phosphorus-sulfur and nitrogen-phosphorus-sulfur fertilizers with insecticidal properties necessary for agriculture.

Processing of phosphorite in the presence of sulfur with incomplete norms of sulfuric acid solution was carried out in a short time, for 15––25 minutes. Since the decomposition reaction is exothermic, it was observed that the temperature was 110–120 °C and higher depending on the sulfuric acid norm. The amount of heat released is used to evaporate excess water in the system, leading to an improvement in the commercial properties of phosphorus-sulfur fertilizers.

Sulfur is normally in the form of a ring with a stable $S_8$ content. At room temperature, as well as as a result of interaction with phosphate minerals, it forms relatively active forms containing $S_2$, $S_3$, $S_4$, $S_5$ and participates in the decomposition of phosphorite.

The amount of sulfuric acid used in the decomposition process is saved by 30–40% by replacing the amount of sulfur in elemental sulfur. An increase in the plant assimilation form of phosphorus in phosphorite samples was observed with increasing sulfur content. The obtained fertilizers contain phosphate minerals in the form of mono- and dicalcium phosphate, and sulfur in the form of $SO_4^{2-}$ -ions and elements. The sulfur in the fertilizer was found to be in a completely hydrophilic form. These data were also confirmed by X-ray and dervatogram analyzes of the new variety of fertilizer. It was found that the decomposition coefficient of phosphorite samples when treated with sulfuric acid in the presence of sulfur is 1.2–1.3 times higher than the decomposition coefficient without the presence of sulfur (with sulfuric acid itself).

The decomposition process was also carried out in the presence of a suspension of sulfuric acid. The preparation of the suspension was carried out in the presence of 75, 80 and 93% solutions of sulfuric acid. As the acid concentration decreases, it becomes more difficult for the sulfur to form a suspension. This is because non-polar molecules of sulfur tend to soak only in non-polar solvents. A decrease in the acid concentration leads to an increase in the mass fraction of water in the solution. Water is a polar molecule.

When the amount of sulfur required for the decomposition of phosphorite is the same, it is practically indistinguishable from the process of decomposition of phosphorite with sulfuric acid suspension, in the presence of phosphorite and sulfuric acid.

Different rates of nitric acid and their decomposition process in the presence of sulfur were studied to obtain insecticidal complex fertilizers containing NPSCa nutrients from low-grade unenriched phosphorites. When phosphorites are processed with nitric acid in the presence of sulfur, the decomposition coefficient is 1.45 times higher than that of a product decomposed without the presence of sulfur.

The change in this indicator can be expressed as follows: the degree of decomposition of unenriched phosphorite flour can be explained by an increase in the amount of $SO_3$ in the fertilizer obtained in the presence of sulfur. For example, when a phosphorite sample is processed at 30% nitric acid without sulfur, it contains 1.65% $SO_3$. When phosphorite is treated with nitric acid by adding 5 and 10% of sulfur, its content is 3.85 and 5.32%, respectively. Nitric acid is not only a source of chemical energy for the decomposition of phosphate minerals in the raw material, but also participates in the process of mutual oxidation-reduction of components in the system (phosphorite, sulfur, nitric acid, moisture, etc.). Under these conditions, the elemental sulfur $S^0$ is oxidized from the oxidation state to $S^{+4}$ ($S^{+6}$) and converted into sulfite and sulfuric acid in the system.

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